EVALUATION OF ATMOSPHERIC IMPACTS OF SELECTED COATINGS EMISSIONS

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OUTLINE

BACKGROUND

- QUANTIFICATION OF REACTIVITY AND EXAMPLES
- UNCERTAINTIES IN REACTIVITY SCALES

REACTIVITY RESEARCH NEEDS FOR ARCHITECTURAL COATINGS

COMPONENTS OF CE-CERT COATINGS PROJECT PROPOSED TO THE CARB

VOC REACTIVITY

VOCs DIFFER IN THEIR EFFECTS ON OZONE FORMATION. THE TERM **REACTIVITY** IS USED TO REFER TO THIS.

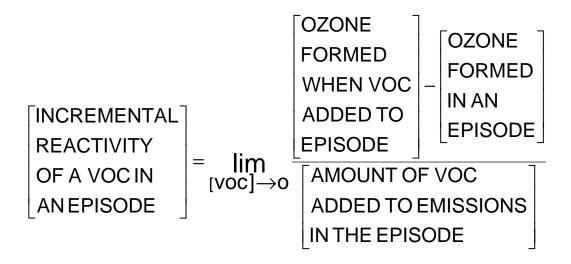
SEVERAL DIFFERENT ASPECTS OF A VOCs ATMOSPHERIC REACTIONS AFFECT ITS REACTIVITY:

- HOW FAST IT REACTS.
- HOW MUCH O3 IS FORMED DIRECTLY FROM ITS REACTIONS AND THOSE OF ITS PRODUCTS.
- WHETHER IT ENHANCES OR INHIBITS ATMOSPHERIC RADICAL LEVELS. THIS AFFECTS HOW FAST O₃ IS FORMED FROM ALL VOCs.
- WHETHER IT ENHANCES RATES NO_x REMOVAL. THIS AFFECTS ULTIMATE O₃ YIELDS BECAUSE NO_x IS REQUIRED FOR O₃ TO BE FORMED.

A VOC'S EFFECT ON O₃ ALSO DEPENDS ON THE NATURE OF THE ENVIRONMENT WHERE IT REACTS.

QUANTIFICATION OF REACTIVITY

A USEFUL MEASURE OF THE EFFECT OF A VOC ON OZONE FORMATION IS **INCREMENTAL REACTIVITY**:



THIS DEPENDS ON THE CONDITIONS OF THE EPISODE AS WELL AS ON THE VOC

MEASUREMENT OR CALCULATION OF ATMOSPHERIC REACTIVITY

REACTIVITY CAN BE MEASURED IN ENVIRONMENTAL CHAMBER EXPERIMENTS. BUT THE RESULTS ARE NOT THE SAME AS REACTIVITY IN THE ATMOSPHERE.

- NOT PRACTICAL TO EXPERIMENTALLY DUPLICATE ALL ATMOSPHERIC CONDITIONS AFFECTING REACTIVITY
- CHAMBER EXPERIMENTS HAVE WALL EFFECTS, USUALLY HIGHER LEVELS OF NOx AND ADDED TEST VOC, STATIC CONDITIONS, ETC.

ATMOSPHERIC REACTIVITY MUST BE CALCULATED USING COMPUTER AIRSHED MODELS, GIVEN:

- MODELS FOR AIRSHED CONDITIONS
- CHEMICAL MECHANISMS FOR THE VOC's ATMOSPHERIC REACTIONS

CALCULATIONS OF ATMOSPHERIC REACTIVITY CAN BE NO MORE RELIABLE THAN THE CHEMICAL MECHANISM USED.

ENVIRONMENTAL CHAMBER EXPERIMENTS ARE USED TO TEST THE RELIABILITY OF MODELS TO PREDICT ATMOSPHERIC REACTIVITY.

EXAMPLES OF WAYS TO DEAL WITH THE DEPENDENCE OF REACTIVITY ON ENVIRONMENTAL CONDITIONS

BASE THE SCALE ON A "REPRESENTATIVE" OR "WORST CASE" EPISODE.

MAY NOT BE OPTIMUM FOR ALL CONDITIONS.

USE MULTIPLE SCALES REPRESENTING THE RANGE OF APPLICABLE CONDITIONS.

- ALLOWS AN ASSESSMENT OF EFFECTS OF VARIABILITY.
- BUT NOT USEFUL WHEN A SINGLE SCALE IS REQUIRED.

BASE THE SCALE ON CONDITIONS WHERE VOCS HAVE MAXIMUM INCREMENTAL REACTIVITIES (**MIR SCALE**).

- REFLECTS URBAN CONDITIONS WHERE OZONE IS MOST SENSITIVE TO VOC EMISSIONS
- GIVES GOOD CORRELATIONS TO EFFECTS OF VOCs ON INTEGRATED OZONE EXPOSURE.
- BUT DOES NOT REPRESENT CONDITIONS WHERE HIGHEST OZONE CONCENTRATIONS ARE FORMED.

EXAMPLES OF RELATIVE REACTIVITIES AT DIFFERENT NO_x LEVELS

OZONE IMPACTS PER GRAM VOC / OZONE IMPACT PER GRAM OF AMBIENT VOC MIXTURE.

COMPOUND OR MIXTURE	MAX. VOC IMPACT (MIR) (HIGH NO _x)	NO _x GIVING MAXIMUM OZONE	**
ETHANE	0.08	0.14	0.17
ALL-ALKANE MINERAL SPIRITS	0.21	0.33	0.30
TEXANOL	0.24	0.32	0.33
ETHYL BENZENE	0.75	0.69	0.50
M-XYLENE	2.9	2.2	1.8
AMBIENT VOC MIXTURE	1	1	1

UNCERTAINTIES IN REACTIVITY SCALES

UNCERTAINTY IN THE GENERAL APPLICABILITY OF ANY SINGLE SCALE

- NO SCALE CAN REPRESENT ALL ENVIRONMENTS.
- NOT ALL EXPERTS AGREE THAT THE MIR SCALE IS THE MOST APPROPRIATE FOR REGULATIONS.
- CALIFORNIA HAS ADOPTED THE MIR SCALE. THE EPA WANTS MORE RESEARCH BEFORE ADOPTING A SCALE FOR REGULATIONS.

CHEMICAL MECHANISM UNCERTAINTY

- GENERAL MECHANISM UNCERTAINTIES CAUSE UNCERTAINTY FOR EVEN WELL-STUDIED VOCs.
- UNCERTAINTIES ARE MUCH GREATER FOR VOCS WITH NO DATA TO VERIFY THEIR MECHANISMS.

COMPOSITION UNCERTAINTY

 APPLICABLE TO COMPLEX MIXTURES SUCH AS VEHICLE EXHAUSTS AND PETROLEUM DISTILLATES

MECHANISM UNCERTAINTY CLASSIFICATION AND MINIMUM UNCERTAINTY ESTIMATES FOR RELATIVE MIR SCALE

NO.	DESCRIPTION	MIN. UNC'Y
1	MECHANISM NOT EXPECTED TO CHANGE SIGNIFICANTLY	15%
2	SOME UNCERTAINTIES BUT MECHANISM ADEQUATELY TESTED	15%
3	ESTIMATED MECHANISM BASED ON DATA FOR SIMILAR COMPOUNDS	30%
4	ESTIMATED MECHANISM BASED ON UNCERTAIN ASSUMPTIONS	75%
5,6	MECHANISM OR ESTIMATE IS HIGHLY SIMPLIFIED OR MAY BE INCORRECT	100%

NOTE:

- MINIMUM UNCERTAINTIES SHOWN ARE HIGHLY APPROXIMATE AND SUBJECTIVE
- UNCERTAINTIES SHOWN ARE FOR RATIOS OF MIRS
- UNCERTAINTIES IN ABSOLUTE OZONE IMPACTS ARE MUCH HIGHER

EXAMPLE SOLVENT VOCs WITH VARIOUS MECHANISM UNCERTAINTY ASSIGNMENTS

NO.	EXAMPLES	MIN. UNC'Y
1	METHANOL, ACETALDEHYDE ^[A] , 1-METHOXY-2-PROPANOL ^[B]	15%
2	ETHYLENE GLYCOL, ETHYLBENZENE, 1-METHOXY-2-PROPYL ACETATE ^[C]	15%
3	C ₈₊ ALKANES ^[D] , MOST GLYCOLS, GLYCOL ETHERS, ESTERS, ETC. ^[E]	30%
4	C ₁₃ NAPHTHALENES, FURAN, C ₃₊ ACETYLENES ^[D]	75%
5,6	AMINES, OXIMES, HALOGENATED COMPOUNDS, OXIMES, ETC. [E]	100%

NOTES:

- [A] SIMPLE, WELL-ESTABLISHED MECHANISMS
- [B] RELEVANT REACTION ROUTES WELL-ESTABLISHED BY LABORATORY STUDIES
- ^[C] ENVIRONMENTAL CHAMBER DATA USED TO VERIFY OR DERIVE MECHANISMS
- [D] MIRS SENSITIVE TO GENERAL MECHANISM UNCERTAINTIES
- [E] MECHANISM UNKNOWN OR VERY UNCERTAIN

EXAMPLES OF COMPOSITIONAL UNCERTAINTY FOR COMPLEX MIXTURES

COMPONENT	MIR UNC'Y
ALL-ALKENE PETROEUM DISTILLATES	
 MINIMAL INFORMATION GIVEN 	~33%
CARBON NUMBER DISTRIBUTIONS KNOWN	~17%
 FRACTIONS OF NORMAL AND TOTAL BRANCHED AND CYCLIC ALSO KNOWN 	0%
MIXTURES OF AROMATICS	
 MINIMAL INFORMATION GIVEN 	~60%
• CARBON NUMBER DISTRIBUTIONS KNOWN	~55%
 FRACTIONS OF MONO-, DI-, AND POLY- SUBSTITUTED BENZENES AND NAPHTHALENES ALSO KNOWN 	0%
OTHERS	
 UNSPECIFIED GLYCOL ETHERS 	~30%
 PETROLEUM DISTILLATE WITH AROMATIC FRACTION NOT SPECIFIED 	~100%

EXAMPLE WORKSHEET TO ESTIMATE OZONE IMPACTS OF A FORMULATION

COMPONENT	GM /LITER	MIR (GM O ₃ / GM)	MIR U COMP	JNC'Y MECH	O ₃ FORM. (GM O ₃ / LITER)
ALKANE MIX	100	0.85	15%	30%	85 ± 29
AROMATIC MIX	10	6.4	50%	30%	64 ± 37
TEXANOL	20	0.89	0	30%	18 ± 5
AMINE	5	~7	0	100%	35 ± 35
UNIDENTIFIED VOCs	2	~4	20	0%	8 ± 16
WHOLE FORMULATION				210 ± 61	

ADDITIONAL INFORMATION AVAILABLE

REACTIVITY RESEARCH WORKING GROUP http://www.cgenv.com/narsto/reactinfo.html

- MISSION STATEMENT
- REACTIVITY POLICY WHITE PAPER
- REACTIVITY SCIENCE ASSESSMENT DOCUMENTS

REACTIVITY DATA AND DOCUMENTATION http://www.cert.ucr.edu/~carter/reactdat.htm

- TABULATION OF MIR, OTHER REACTIVITY SCALES
- REPORT DOCUMENTING CHEMICAL MECHANISM AND METHODS USED TO CALCULATE REACTIVITY
- LINKS TO OTHER REPORTS AND PRESENTATIONS CONCERNING W.P.L. CARTER'S RESEARCH

REACTIVITY RESEARCH NEEDS FOR VOCs FOR ARCHITECTURAL COATINGS

REACTIVITY DATA ARE ALREADY AVAILABLE FOR MANY TYPES OF VOCs USED IN COATINGS

- DATA AVAILABLE FOR REPRESENTATIVE ALKANES, AROMATICS, ALCOHOLS, GLYCOLS, ESTERS, ESTERS AND A FEW OTHERS.
- BUT NOT ALL ASPECTS OF MECHANISMS ARE ADEQUATELY EVALUATED.

REACTIVITY ESTIMATES ARE UNCERTAIN FOR SOME IMPORTANT TYPES OF COATINGS VOCs

- NO DATA FOR LOW VOLATILITY COMPOUNDS SUCH AS TEXANOL
- PETROLEUM DISTILLATES HAVE LARGE COMPOSITIONAL UNCERTAINTY
- COATINGS INCLUDE COMPOUNDS WITH VERY UNCERTAIN REACTIVITY ESTIMATES
 - UNSATURATED OXYGENATES SUCH AS VINYL ACETATE AND ACRYLATES.
 - AMINES AND ALCOHOL AMINES

NEED TO DEVELOP LOWER COST REACTIVITY SCREENING AND ENFORCEMENT METHODS

UNCERTAIN HOW MUCH DEPOSITION ON SURFACES AND OTHER NON-ATMOSPHERIC LOSS PROCESSES ARE AFFECTING ATMOSPHERIC AVAILABILITY

COMPONENTS OF CE-CERT COATINGS PROJECT FOR THE CARB

CONDUCT EMISSIONS, REACTIVITY AND UNCERTAINTY SURVEY OF COATINGS VOCs TO PRIORITIZE RESEARCH

CONDUCT ENVIRONMENTAL CHAMBER STUDIES OF SELECTED COATINGS VOCs USING "NEXT GENERATION" CHAMBER BEING DEVELOPED FOR THE EPA

APPLY A DIRECT REACTIVITY SCREENING METHOD TO LOW VOLATILITY VOCs, PETROLEUM DISTILLATES, OTHER COATINGS CONSTITUENTS

DEVELOP AND EVALUATE IMPROVED PROCEDURES TO QUANTIFY REACTIVITIES AND COMPOSITIONAL UNCERTAINTIES FOR PETROLEUM DISTILLATES

HOWEVER, AVAILABLE FUNDING NOT SUFFICIENT TO DO ALL THE WORK NEEDED IN THESE AREAS.

PRELIMINARY RESULTS OF SURVEY OF COATINGS EMISSIONS REACTIVITY

VOCs IN DRAFT COATINGS INVENTORY FOR WHICH REACTIVITY DATA ARE UNAVAILABLE

MIR x EMIT	TYPE OF VOC	MECH UNC'Y	
WATER BASED COATINGS			
~10%	Texanol	3	
~5%	Vinyl Acetate	5	
~5%	Butyl Carbitol	3	
~3%	Various Petroleum Distillates	-	
~1%	Methyl Carbitol	3	
~0.5%	Diethylene Glycol	3	
~0.5%	Di (propylene glycol) Methyl Ether	3	
~0.5%	2-Amino-2-Methyl-1-Propanol	6	
~25%	UNCERTAIN VOC TOTAL		
SOLVENT BASED COATINGS			
~50%	Various Petroleum Distillates	-	
~1%	n-Butyl Alcohol	3	
~0.5%	Ethyl 3-Ethoxypropionate	3	
~50%	UNCERTAIN VOC TOTAL		

ENVIRONMENTAL CHAMBER STUDIES OF SELECTED COATINGS VOCs

VOCs WILL BE CHOSEN BASED ON RESULTS OF SURVEY

 TEXANOL APPEARS TO BE A PRIORITY, BUT VINYL ACETATE SHOULD ALSO BE CONSIDERED

NEW LARGE ENVIRONMENTAL CHAMBER BEING DEVELOPED FOR THE EPA WILL BE EMPLOYED

- CONSTRUCTED AND EVALUATED USING ~\$3 MILLION FUNDING FROM CONGRESS
- CAN OBTAIN DATA AT LOWER CONCENTRATIONS THAN PREVIOUSLY POSSIBLE
 - MORE REPRESENTATIVE OF CURRENT AMBIENT ATMOSPHERES
 - EASIER TO STUDY LOW VOLATILITY VOCs
- INSTRUMENTATION FOR MORE COMPREHENSIVE CHEMICAL ANALYSIS
- INSTRUMENTATION FOR INFORMATION ON AEROSOL (PM) IMPACTS

METHODS FOR STUDIES OF LOW VOLATILITY VOCS WILL BE INVESTIGATED IF NEEDED

BECAUSE OF LIMITED FUNDING, ONLY A SINGLE COMPOUND CAN BE STUDIED

U.C. RIVERSIDE CHAMBER FACILITY PROGRESS AND CURRENT STATUS

INTERNATIONAL WORKSHOP ON ATMOSPHERIC CHEMISTRY AND ENVIRONMENTAL CHAMBER RESEARCH HELD IN OCTOBER, 1999

EXPERIMENTS UNDERWAY TO INVESTIGATE AND MINIMIZE BACKGROUND EFFECTS USING SMALLER (~3000-LITER) REACTORS

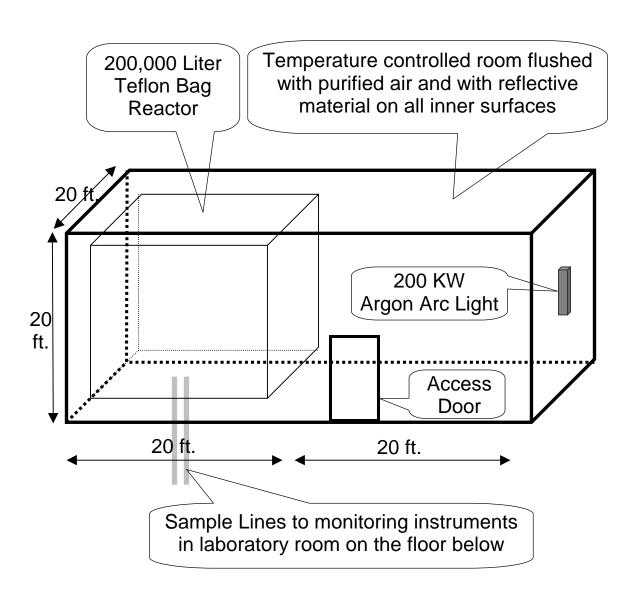
- VARIOUS TYPES OF WALL MATERIAL TESTED
- BACKGROUND NO_x OFFGASING ~1 PPB/DAY

OBTAINING INSTRUMENTATION MOST NEEDED FOR ASSESSING LOW NO_x EFFECTS

DESIGN AND CONSTRUCTION OF CHAMBER AND LIGHT SOURCE FACILITY

- DESIGN WORK COMPLETED
- NEW BUILDING BEING CONSTRUCTED. ESTIMATED COMPLETION MARCH, 2001
- 200,000-LITER TEFLON BAG REACTOR(S) WILL BE IN "CLEAN ROOM" FLUSHED WITH PURE AIR
- 200 KW ARGON ARC LIGHT WILL SIMULATE SUNLIGHT SPECTRUM AND INTENSITY
- TEMPERATURE CONTROL FROM 4 50°C (40 - 120°F) TO ±1°C (±2°F)
- EXPECTED TO BE OPERATIONAL IN MAY, 2001

DIAGRAM OF ENVIRONMENTAL CHAMBER AND TEMPERATURE-CONTROLLED ENCLOSURE



DEVELOPMENT AND APPLICATION OF DIRECT REACTIVITY SCREENING METHOD

DIRECT REACTIVITY

- THIS IS THE RATE A VOC REACTS AND OXIDIZES NO, WHICH IS THE PROCESS THAT FORMS O₃
- THIS IS ONE OF SEVERAL FACTORS AFFECTING REACTIVITY. THIS MAY BE MORE IMPORTANT IN THE ATMOSPHERE THAN IN CHAMBER STUDIES.
- MEASURES OF DIRECT REACTIVITY WILL GIVE MORE COMPLETE MECHANISM EVALUATION AND CAN TEST UNCERTAIN REACTIVITY ESTIMATES.

OBJECTIVES

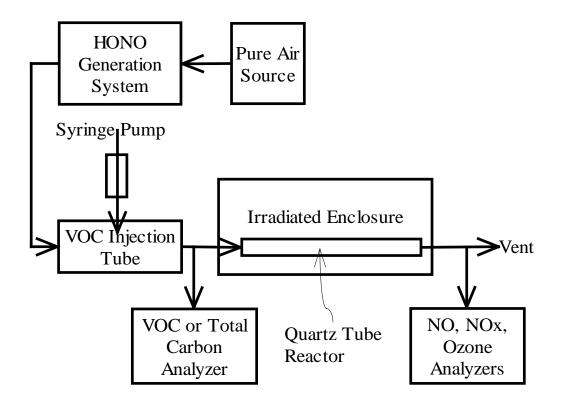
- DEVELOP A MEANS TO MEASURE DIRECT REACTIVITY THAT IS LESS EXPENSIVE AND AMBIGUOUS THAN CHAMBER STUDIES.
- ADAPT THE METHOD SO IT CAN BE USED FOR LOW VOLATILITY COMPOUNDS AND FOR COMPLEX MIXTURES.
- APPLY THE METHOD TO TEST MECHANISMS OF SELECTED VOCs
- APPLY METHOD TO TEST REACTIVITY ESTIMATION METHODS FOR PETROLEUM DISTILLATES
- APPLY METHOD TO TEST REACTIVITY ESTIMATION METHODS FOR WHOLE SOLVENTS OR COATINGS?

PRINCIPLE OF DIRECT REACTIVITY MEASUREMENT METHOD

PHOTOLYSIS OF NITROUS ACID (HONO) IN THE PRESENCE OF ADDED VOC IN AIR

- IN ABSENCE OF ADDED VOC, HONO/AIR PHOTOLYSIS FORMS MAINLY NO AND NO2
- ADDED VOC CAUSES NO TO DECREASE AND O₃ TO BE FORMED IF ALL THE NO IS CONSUMED
- CHANGE IN [O₃]-[NO] CAUSED BY ADDING VOC IS THE MEASURE OF DIRECT REACTIVITY

FLOW SYSTEM EMPLOYED



CURRENT STATUS OF WORK ON DIRECT REACTIVITY MEASUREMENT METHOD

METHOD BEING DEVELOPED FOR AN EXISTING CARB CONTRACT THAT ENDS IN 12/2001

METHOD TESTED SUCCESSFULLY WITH N-ALKANES THROUGH N-C16.

NEED TO TEST REPRODUCIBILITY OF THE METHOD AND APPLICABILITY TO OTHER COMPOUNDS.

SYRINGE PUMP INJECTION METHOD MAY PERMIT EVALUATION OF COMPLEX MIXTURES AND LOW VOLATILITY MATERIALS

NEED TO DEVELOP TOTAL CARBON ANALYSIS METHOD FOR COMPLEX MIXTURES AND LOW VOLATILITY MATERIALS

WORK FOR PROPOSED PROGRAM

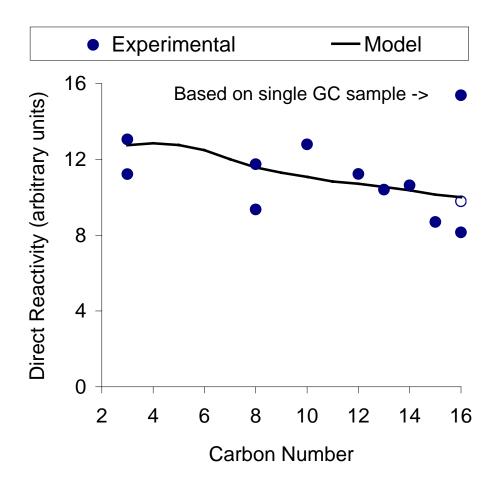
AMOUNT OF DEVELOPMENT WORK REQUIRED ON COATINGS PROGRAM WILL DEPEND ON STATE OF PROGRESS WHEN EXISTING CONTRACT ENDS.

APPLICATION TO TEXANOL AND OTHER LOW VOLATILITY COATINGS MATERIALS

APPLICATION TO PETROLEUM DISTILLATES

APPLICATION TO WHOLE COATINGS EMISSIONS?

CURRENT STATUS: DIRECT REACTIVITY MEASUREMENT RESULTS FOR NORMAL ALKANES



REACTIVITY QUANTIFICATION FOR PETROLEUM DISTILLATES

CURRENT STATUS

- PETROLEUM DISTILLATES ARE MAJOR COMPONENTS OF SOLVENT-BASED COATINGS
- FOLLOWING COMPOSITIONAL INFORMATION IS REQUIRED FOR REACTIVITY ESTIMATES:
 - ALKANE AND AROMATIC CONTENT
 - CARBON NUMBER DISTRIBUTION
 - NORMAL, BRANCHED AND CYCLIC ALKANE DISTRIBUTION
 - AROMATIC SPECIATION, IF APPLICABLE
- ESTIMATES CONSISTENT WITH CHAMBER DATA FOR THE FEW MIXTURES THAT WERE STUDIED.
 BUT REPRESENTATIVENESS IS UNCERTAIN.
- NECESSARY COMPOSITIONAL INFORMATION DIFFICULT TO OBTAIN AND OFTEN PROPRIETARY
- CARB STAFF DEVELOPED PROTOCOL FOR MAKING MIR ESTIMATES BASED ON LIMITED DATA
 - NOT EXPERIMENTALLY EVALUATED
 - BASED ON PROPRIETARY DATA
 - NO PROVISION FOR CHANGING OR UPDATING REACTIVITY SCALE.
 - NO PROVISION FOR COMPOSITIONAL UNCERTAINTY ANALYSIS.

REACTIVITY QUANTIFICATION FOR PETROLEUM DISTILLATES

PROPOSED PROJECT

- DEVELOP SPREADSHEET-BASED METHOD TO ESTIMATE REACTIVITY AND COMPOSITIONAL UNCERTAINTY FOR PETROLEUM DISTILLATES
 - ESTIMATES IN TERMS OF COMPOSITION SO ANY REACTIVITY SCALE CAN BE USED
 - ESTIMATES WHEN DATA LIMITED BASED ON AVAILABLE COMPOSITION DATA
 - UNCERTAINTY ESTIMATES WILL BE A FUNCTION OF AMOUNT OF INFORMATION
 - SPREADSHEET DOCUMENTED FOR USE BY INDUSTRY AND REGULATORS
- EVALUATE METHOD
 - COMPARING ESTIMATES WITH DETAILED COMPOSITION DATA WHERE AVAILABLE
 - COMPARING PREDICTED <u>VS</u> MEASURED DIRECT REACTIVITIES
 - COMPARING PREDICTIONS WITH CHAMBER DATA WHERE DATA AVAILABLE
- INDUSTRY PARTICIPATION IS ESSENTIAL TO OBTAIN NECESSARY INFORMATION
 - NEED TO DEVELOP PROCEDURES TO ALLOW USE OF PROPRIETARY DATA TO DEVELOP AND EVALUATE METHOD